

COEFFICIENTS OF SEPARATION OF ISOTOPES AND THE MECHANISM OF THE LIBERATION OF HYDROGEN

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UDC 541.138.3:546

The relationship of the coefficients of separation of isotopes of individual stages of the process to the summary measurable effect is discussed. It was shown that in the case of activationless occurrence of the reaction of electrochemical desorption, the experimentally observed values of the coefficient of separation unambiguously indicate a substantial difference in the pre-exponential factors in the rate constant of this reaction for different isotopes. The influence of the difference of the zero energies upon the coefficient of separation at the stage of discharging was calculated within the framework of the theory of hydrogen overvoltage of Dogonadze, Kuznetsov, and Levich. A comparison of these calculations with the experiment also makes an appreciable difference of the pre-exponential factors at this stage as well probable.

The question of the relationship of the coefficients of separation of hydrogen isotopes to the mechanism of the electrode reaction has been paid considerable attention in recent years (surveys of the studies are given in [1-4]; see also [5]). It is important to note here that the experimentally measured coefficient of separation represents a quantity characterizing the process as whole, and not any one step of it. The corresponding functions were analyzed by Bockris and Srinivasan [6]. Since, however, the conclusions of [6] were drawn on the assumption of quite definite kinetic principles, in particular, the same nature of the dependence of the rates of discharging and electrochemical desorption on the potential, we consider it advisable to reconsider this question in more general form.

Let us consider the conditions of sufficiently high cathodic polarization, when both processes—discharging and electrochemical desorption—occur practically irreversibly; i.e., the reverse reactions can be neglected. Then the rate of conversion of atoms of a given type, for example, H atoms to a gas (i_H), will be equal to the rate of their removal from solution both by discharging (i_{di_H}) (the adsorbed H atoms formed in this case are no longer returned to the solution) and by electrochemical desorption (i_{de}):

$$i_H = i_{di_H} + i_{de_{H-H}} + i_{de_{D-H}} \quad (1)$$

Here $i_{de_{H-H}}$ denotes the current of desorption of the adsorbed H atom in the reaction with H^+ from solution; $i_{de_{D-H}}$ is the same for the reaction of $D+H^+$. Analogously, the current of transition of deuterium from solution into gas comprises

$$i_D = i_{di_D} + i_{de_{H-D}} + i_{de_{D-D}} \quad (2)$$

The coefficient of separation S is determined in terms of the corresponding currents and summary concentrations of the isotopes C_H and C_D , as

$$S = \frac{i_H}{i_D} \cdot \frac{C_D}{C_H} \quad (3)$$

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Élektrokhimiya*, Vol. 6, No. 10, pp. 1456-1461, October, 1970. Original article submitted April 16, 1968.

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If the deuterium concentration is much less than the protium concentration, then formulas (1) and (2) are substantially simplified. Under these conditions $i_{deD-H} \ll i_{deH-H}$ and $i_{deD-D} \ll i_{deH-D}$, so that the corresponding components can be neglected. Moreover, subsequently in the consideration of one reaction or another we can in practice limit ourselves to a consideration of only one molecular form of proton or deuterium donor—for example, for D only H_2DO^+ —and neglect HD_2O^+ , etc.

After simplification, (1) and (2) take the form

$$i_H = i_{diH} + i_{deH-H}, \quad (1a)$$

$$i_D = i_{diD} + i_{deH-D}. \quad (2a)$$

The currents of discharging and desorption are related by the equations of equilibrium of the surface concentration of the corresponding types of ions:

$$i_{diH} = i_{deH-H} + i_{deH-D} \approx i_{deH-H}, \quad (4)$$

$$i_{diH} = i_{deD-H} + i_{deD-D} \approx i_{deD-H}. \quad (5)$$

It is important that (4) relates the same quantities that are contained in (1) and (1a), whereas the currents determining i_D are practically not related to one another by any conditions [cf. (2a) and (5)]. This difference is understandable, since the reactions with H are the basic reactions, creating the background against which the processes with the participation of deuterium occur. As a result, one of the two basic processes leading to the transition of deuterium to the gas, i_{deH-D} , is found to have no relationship at all to the coverage of the surface by deuterium.

Substituting (1a), (2a), and (4) into (3), we obtain

$$S = 2 \left/ \left(\frac{1}{S_{di}} + \frac{1}{S_{de}} \right) \right. = \frac{2S_{di}S_{de}}{S_{di} + S_{de}}. \quad (6)$$

Here the coefficients of separation of the steps of discharging $S_{di} = (i_{diH}/i_{diD}) \cdot (c_D/c_H)$ and electrochemical desorption $S_{de} = (i_{deH-H}/i_{deH-D}) \cdot (c_D/c_H)$ were introduced. Let us emphasize that the latter coefficient pertains not to any process of desorption, but to the reaction of the adsorbed protium atom with the source of protons or deuterons, while the ratio of the rate constants $(H+H^+)/(D+D^+)$, $(H+H^+)/(D+H^+)$ or $(D+H^+)/(D+D^+)$ has no effect on the experimentally determined value.

Equation (6) practically coincides with the expression obtained by Bockris and Srinivasan [6].* As can be seen from the above-mentioned, its derivation does not require concretization of the nature of the dependence of the current on the potential, the nature of the discharging particles, and the slow step of the process.

Let us consider the separation of the isotopes in the liberation of hydrogen from acid solutions. Under these conditions the discharging current is entirely determined by the discharging of hydroxonium ions. For further consideration it is convenient to introduce the true coefficient of separation at the step of discharging $S_{di}' = (i_{diH}/i_{diD}) \cdot (c_D'/c_H') = (S_{di}/K)$. Here c' represents the concentrations of the corresponding isotope in hydroxonium ions, while $K = (c_H'/c_D') \cdot (c_D/c_H)$ is the coefficient of separation, determined by the equilibrium distribution of the isotopes between hydroxonium ions and water.† The general coefficient of separation

*In [6] an equation analogous to (6) was obtained. The difference between them is due to the fact that, in contrast to the definition of S_{de} that we used, Bockris and Srinivasan call a quantity twice as large the coefficient of separation of the step of desorption, while for the step of discharging the expression in (6) coincides with ours.

†Strictly speaking, still another factor $(1+3/2x)/[1+(3/2)(x/K)]$, considering the deviation of the ratio of the summary concentrations of the isotopes from the ratio of their concentrations only in water molecules (here x is the ratio of the number of hydroxonium ions to the number of water molecules), should have been introduced into the expression for K . However, in a 1 M solution of acid ($x \approx 0.02$), this factor is only 1.01, and therefore will not be considered henceforth (the value $K=1.45$ follows from the data cited in the survey [7]; for tritium, considering the ratio of the reduced masses, we obtain $K=1.70$).

for discharging S_{di} is naturally determined the product of the coefficients of separation at the step of transfer of protons (deuterons) from water molecules to hydroxonium ions and at the step of discharging of the corresponding ions.

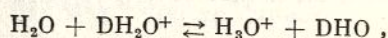
As for the reaction of electrochemical desorption, as we have recently shown [8], for metals with a high hydrogen overvoltage (of the type of mercury) the main source of protons [in a ratio $\sim (1-x)/x$] here is water molecules, so that the correction for the value of K is not required, and, consequently, the coefficient S_{de} entering into formula (6) represents the true kinetic value S_{de}' .

The values of the true kinetic coefficients of separation represent none other than the ratio of the rate constants of the corresponding reactions: $S_{di} = K_{diH}/K_{diD}$ and $S_{de}' = K_{deH-H}/K_{deH-D}$. This ratio of the constants is determined by the exponent of the difference of the activation energies (ΔE) and the ratio of the pre-exponential factors (S^*), for example, $S_{di} = S_{di}^* \exp(\Delta E_{di}/RT)$.

The difference of the activation energies is determined by the difference of the values of the change in the zero energy from the initial state to the activated state. In a number of studies (see [1-4]) an estimate was made of the properties of the activated state within the framework of the model of Horiuchi and Polanyi; i.e., the activated state was considered as such when hydrogen was bonded both to oxygen and to the metal, and these bonds were greatly shifted in comparison with their equilibrium lengths. Rather complex calculations of the zero energies of the activated state proved to be extremely sensitive to the selection of the details of the model and did not lead to entirely reliable results.

At the present time, the possibility has emerged for reexamining this question from the standpoint of the new theory of hydrogen overvoltage, developed by Dogonadze, Kuznetsov, and Levich [9]. According to this theory, a large value of the vibrational quantum of covalent bonds of hydrogen leads to the fact that the excitation of the vibrations of the OH bond, i.e., the mechanism of discharging of Horiuchi and Polanyi, proved to be extremely improbable. Thermal vibrations of the solvent molecules, occurring practically classically, lead to a fluctuation of the polarization. When, as a result of these fluctuations, the energies of the initial and final states (vibrationally excited according to intermolecular degrees of freedom of the solvent, but without excitation of the vibrations of covalent bonds) are comparable, then there is a simultaneous quantum mechanical jumpover of a proton and electron, and the system passes from the initial to the final state. Thus, in this theory the change in the zero energy during the process of discharging is equal to the difference of the zero energies of the initial (hydroxonium ion) and final (adsorbed atom) states. The corresponding value can be calculated with sufficiently high accuracy.

The spectra of the H_3O^+ ion (and, all the more, DH_2O^+) have not been studied in such detail as to be able to perform an entirely rigorous calculation of the zero energies.* However, sufficiently reliable figures can be obtained in the following roundabout way. The equilibrium coefficient of separation K , equal to $3/2 K_{eq}$, where K_{eq} is the equilibrium constant of the reaction



is known (the factor $3/2$ takes into consideration the conversion from concentrations of the molecules in K_{eq} to the concentrations of atoms in K).

The free energy of this reaction is equal to the difference of the zero energies $\Delta \epsilon = \epsilon_{DHO} + \epsilon_{H_3O^+} - \epsilon_{H_2O} - \epsilon_{DH_2O^+}$ with a correction for the entropy factor, considering the fact that two equivalent places in the water molecule are provided for replacement by deuterium, while there are three in the hydroxonium ion (if $\Delta \epsilon = 0$, then K_{eq} would be equal to $2/3$).

From this we find

$$\exp \frac{\epsilon_{DH_2O^+} - \epsilon_{H_3O^+}}{RT} = \frac{3}{2} K_{eq} \exp \frac{\epsilon_{DHO} - \epsilon_{H_2O}}{RT}. \quad (7)$$

*We did perform the corresponding estimates, bringing in analogies with the spectrum of the ammonia molecule; these gave results close to those cited below.

There are no direct data on the spectra of hydrogen adsorbed on mercury and other metals.* Earlier [10] we found an empirical law relating the frequency of the valence vibration to the energy of the bond of the corresponding hydride and consequently permitting the zero energy of this vibration to be expressed in the function of the energy of the bond:

$$\varepsilon_{M-H} = 0,042E_{M-H}. \quad (8)$$

The corresponding values for deuterium and tritium can easily be found by dividing by the root of the reduced mass ($\sqrt{2}$ or $\sqrt{3}$).

In the case of the formation of an adsorption bond, not only a valence vibration at this bond, but also a doubly degenerate† deformational vibration appears.‡ Its frequency is subject only to an approximate estimate. A comparison of the data for a large number of polyatomic hydrides shows that the frequencies of the valence vibrations are always more than twice as great as the frequencies of the deformational vibrations (this ratio usually does not exceed 2.5). Therefore we assumed that the frequency of the deformational vibration is half as great as that of the valence vibration, i.e., the zero energy of these two vibrations is equal to the energy estimated according to (8).

We should emphasize that, at least for metals of the type of mercury, the bond of adsorbed hydrogen is weak, and the corresponding zero energy is low. Thus, for mercury $E_{M-H} - \varepsilon = 29$ kcal [11], from which $\varepsilon_{Hg-H} = 2.56$ kcal, $\varepsilon_{Hg-D} = 1.88$ kcal, $\varepsilon_{Hg-T} = 1.53$ kcal, i.e., the differences of interest to us, $\varepsilon_{HgH} - \varepsilon_{HgD} = 0.78$ kcal and $\varepsilon_{HgH} - \varepsilon_{HgT} = 1.13$ kcal. It is clear that even a substantial percent error in these values does not lead to very large errors in the final result (for example, a 30% error changes S_{di}^E by approximately 1.2-fold).

In the theories of the Horiuchi-Polanyi type, the value of the zero energy has no effect on the mutual arrangement of the potential curves, influencing only the level of reading of the activation energy. In the theory of Dogonadze et al., however, the value of the zero energy has a direct influence on the relative arrangement of the electron-proton terms. Therefore the zero energies enter into the expression for the activation energy just like the remaining components of the energy difference of the initial and final states, i.e., with the coefficient α . Thus

$$S_{di}^E = \exp \alpha \frac{\varepsilon_{H_2O} - \varepsilon_{DHO} + (\varepsilon_{M-H} - \varepsilon_{M-D})}{RT} = K^{-\alpha} \exp \alpha \frac{\varepsilon_{H_2O} - \varepsilon_{DHO} - (\varepsilon_{M-H} - \varepsilon_{M-D})}{RT}. \quad (9)$$

The difference $\varepsilon_{H_2O} - \varepsilon_{DHO}$ can be determined from data on the heats of dissociation of $HO-H$ and $HO-D$. It is equal to 1.7 kcal, and for the corresponding tritium compound 2.5 kcal [12].** As a result of the calculation we obtain $S_{di}^E = 1.8$ for deuterium and $S_{di}^E = 2.4$ for tritium; the corresponding values of the product KS_{di}^E , entering into the final formula for S , are 2.6 and 4.1.

The energy ratios for the electrochemical desorption on a mercury cathode are such that this process should proceed without activation [8, 11]. Since the activation energy for it is equal to zero, the difference in the zero energies does not play any role, and, consequently, $S_{de}^E = 1$. Considering this result, we obtain from formula (6)

$$S = \frac{2KS_{di}^E S_{di}^{\kappa} S_{de}^{\kappa}}{KS_{di}^E S_{di}^{\kappa} + S_{de}^{\kappa}} \quad (6a)$$

*The use of data on the gaseous hydride HgH here is apparently unjustifiable, since the bond in it belongs to an excited Hg atom, which is null-valent in the free state. The use of this frequency in the calculation would lead to a decrease in S_{di}^E .

†Two deformational vibrations may also have a different frequency if the adsorption center possesses low symmetry.

‡In the case of stripping of H from H_3O^+ , one valence and two deformational vibrations also disappear. In the reaction $M + H_3O^+ + e \rightarrow M-H + H_2O$, the number of particles capable of independent translational and rotational motion does not change; therefore the total number of vibrational degrees of freedom is also maintained.

**A calculation of these values according to the data pertaining to molecules of a different isotopic composition gives results coinciding within 0.1 kcal.

Evidently at any high value of S_{di}^E (and S_{di}^{κ}), the summary coefficient as separation cannot exceed $2S_{de}^{\kappa}$. The fact that $S > 2$ is always observed experimentally shows that $S_{de}^{\kappa} > 1$, i.e., there is a substantial difference of the pre-exponential factors for processes in which the light and heavy isotopes participate. It is important to emphasize that this conclusion is related only to the activationless character of the desorption process and does not depend on the estimates of S_{di}^E made above.

Possibly for the process of discharging also $S_{di}^{\kappa} > 1$ (this follows from a comparison of the value of S according to formula (6a) with the experimental value, considering the estimates of S_{di}^E made above, if we assume that S_{di} is not negligible in comparison with S_{de}).

The conclusions of an appreciable difference of the pre-exponential factors agree with the fact that, as was shown in [11], the pre-exponential factors in the discharging of hydrogen ions on a mercury cathode are significantly below the theoretical values, i.e., the transmission coefficient $\kappa < 1$. Therefore it is quite reasonable to assume that these deviations differ from H and D.

From the data of Post and Hiskey [13] it is known that the pre-exponential factor for the discharging of D_3O^+ in D_2O as the solvent is twice as great as for the discharging of H_3O^+ from a solution in normal water. This seems to contradict the conclusion drawn above, that it is most probable that $S_{di}^{\kappa} > 1$; i.e., the pre-exponential factor is greater for protium. It should, however, be taken into consideration that the data cited above pertain to real pre-exponential factors (comparison at constant overvoltage), while the ratio of the ideal values is important for these coefficients of separation—the process occurs at the same potential drop for both isotopes. The corresponding evaluation shows that actually this ratio is somewhat greater than one [2]. Moreover, a direct comparison of the data of Post and Hiskey with the data on the coefficients of separation is scarcely justified. Actually, the first data pertain to ions existing in different media and, in all probability, at different distances from the electrode, which can substantially influence the degree of overlapping of the wave functions, while for the second case—a comparison of H_3O^+ and DH_2O^+ in the same medium—the differences in this respect are probably less substantial.

It is known that the coefficient of separation of isotopes generally depends on the electrode potential. As can be seen from the calculation cited above, the value of S_{di}^E , determined by the difference in the zero energies of the initial and final states, does not depend on the potential.* Therefore the main contribution to the change in the coefficient of separation with the potential is made by the change in S^{κ} . This value can be changed on account of a slight approach of the hydroxonium ions toward the electrode as the potential is increased and the associated increase in the overlapping of the wave functions of hydrogen and the hydroxonium ion in the adsorbed state as well. The possibility of such an explanation was noted by R. R. Dogonadze and A. M. Kuznetsov, to whom I should like to express my gratitude for their useful discussions of the questions considered in this article.

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*If we do not assume any appreciable deformation of ions and a corresponding change in the zero energies with increasing potential.